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(54) Title: METHOD OF CONTROLLING MICROBIAL FOULING IN AQUEOUS SYSTEM

(57) Abstract: Disclosed is a method of controlling microbial fouling in an aqueous system of pH 6.5 to 9.5, which is capable of effectively inhibiting slime attachment to a submerged surface simultaneously with killing microorganisms by adding to the aqueous system predetermined amounts of a chlorine biocide, a sulfamate ion source and a water-soluble bromide ion source.

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METHOD OF CONTROLLING MICROBIAL FOULING IN AQUEOUS SYSTEM

TECHNICAL FIELD

The present invention relates, generally, to a method of controlling microbial fouling in an aqueous system. More particularly, the present invention relates to a method of eliminating microorganisms in an aqueous system, which is based on a detachment of slime formed in the aqueous system using a chlorine biocide, a sulfamate ion source and a water-soluble bromide ion source.

PRIOR ART

Water systems, such as cooling towers installed in factories or buildings, have the most optimal environment for the growth and proliferation of microorganisms. Especially, in case of cooling towers in public buildings, pathogens such as *Legionella* bacteria may be rapidly spread, and all people coming in and out the building are thus exposed to, especially, the potentially lethal *Legionella*. In addition, such microbial contamination often leads to the formation of slime in cooling towers. Especially, when formed in cooling towers in factories, slime gives rise to significant problems, as follows: cooling water velocity drops and heat transfer efficiency is reduced resulting in energy loss; oxygen is depleted under slime layers, and anaerobic bacteria cause pitting corrosion on heat exchanger surfaces which leads to heat exchanger replacement .

In order to solve these problems, microbicides are used in aqueous systems that are liable to contamination with microorganisms, such as cooling towers. Among microbicides, oxidizing chlorine biocides are widely used for economic benefits. However, , chlorine biocides have several problems such as reduced effects on control of the growth of microorganisms in the water

contaminated by ammonia, air pollution and offensive odor problem by high volatility, increased corrosivity with increased concentration in water, etc. In this regard, in case of small cooling towers installed in buildings, expensive non-oxidizing biocids such as isothiazolone can be used, which have low corrosiveness and excellent effects on control of microorganisms when it is used above MIC (Minimum Inhibition Concentration). However, they have a potential of causing burns on the skin when contacting with the skin, and are frequently used below MIC due to high costs, resulting in the reduction of their effects on controlling microbial growth.

Disinfection efficiency of microbiocides applied to aqueous systems is typically analyzed by adding a microbiocide to an aqueous system, collecting water from the aqueous system, performing microorganism culturing and counting the cell number. However, even in case that microorganisms are detected at low levels, slime often forms in aqueous systems. This phenomenon is induced by mainly sessile bacteria. In detail, microorganisms are, according to their habitats, classified into planktonic bacteria freely floating in water and sessile bacteria attached to surfaces. With this respect, the conventional method cannot easily detect sessile bacteria directly participating in the production of slime, while detecting only planktonic bacteria. In fact, slime is responsible for many problems associated with microbial contamination. For example, when a microbicide is applied to cooling towers to eliminate *Legionella* bacteria most lethal in public buildings, only suspending bacteria are killed, while bacteria present in slime remain viable. Therefore, diverse bacteria inhabiting in slime proliferates again with time. In addition, several problems such as unpleasant odor and damaged beauties originate mostly from slime.

To date, such slime was removed by using high-pressure water after periodically stopping operations of aqueous systems. However, such a physical method is very cumbersome and costly, especially for large chemical factories because of the reduced operation time. An alternative method for removing slime without stopping operations of aqueous systems is to add excessive chlorine to

aqueous systems. However, such high concentrations of chlorine causes significant problems such as increase of corrosion rates and generation of unpleasant odor, and thus use of chlorine is actually impossible. Also, removal of slime may be achieved by continuous use of non-oxidizing biocides such as isothiazolone of over MIC, but this method is uneconomical.

On the other hand, sulfamic acid, a white crystal that is not volatile, not moisture-absorptive and odorless, is used for metal cleaning, descaling, etc. due to its property of being a strong acid when dissolved in water. Sulfamate salts are used for preparation of flame retardants or weed-controlling agents, and also utilized as a stabilizer for chlorine. In case of being used for descaling, sulfamic acid is used in the form of being dissolved in water, that is, an acidic aqueous solution. The sulfamic acid solution has a remarkably lower corrosiveness to metals than hydrochloric acid and sulfuric acid solutions. This relatively weak corrosiveness of the sulfamic acid solution results from that sulfamic acid reacts with most metals to produce sulfamate salts with a low corrosiveness to metals. Also, sulfamic acid is an amphoteric compound that can act as either an acid or a base, and, thus, its nature changes according to pH. Further, sulfamic acid easily reacts with other compounds. However, sulfamic acid's nature was not completely identified.

When sulfamic acid is used as a stabilizer for chlorine, volatility of chlorine is greatly reduced, whereas its rapid-acting disinfection efficacy is reduced. Such reduced disinfection efficacy of chlorine upon use of sulfamic acid is described by Stuart et al., "Swimming Pool Chlorine Stabilizers" Soap and Chemical Specialties, Aug. 1964. According to this publication, in an aqueous system containing hypochlorite (free residual chlorine level of 0.6 ppm) sufficiently expected to have disinfection efficacy, when sulfamic acid is used as a stabilizer in low concentrations (0.5 to 1.0 ppm), disinfection efficacy of hypochlorite is rarely reduced, whereas hypochlorite almost loses its disinfection efficacy when the concentration of sulfamic acid is increased over the range (25 to 50 ppm).

Efforts to use chlorinated sulfamic acid as a microbicide were made, as described in U.S. Pat. No. 3,328,294 granted to Self et al., U.S. Pat. No. 3,767,586 granted to Rutkiewic et al., etc. The chlorinated sulfamic acid was used as a microbiocide in certain fields such as cooling towers, but is currently limited in use due to its low rapid-acting disinfection efficacy.

On the other hand, in an aqueous system of high pH or containing amines, bromine is superior in limiting microbial growth to chlorine. For this reason, hypobromite produced by reacting hypochlorite with a water-soluble bromide ion is often utilized in such an aqueous system. However, since the hypobromite is not stable and thus impossible to be stored, a hypochlorite solution and a water-soluble bromide solution are typically mixed to generate hypobromite immediately before being added to an aqueous system. U.S. Pat. No. 4,759,852 (hereinafter, referred to as simply '852 patent) granted to Trulear et al. discloses a method of producing hypobromite according to the following reaction formula.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$Br^- + HOCl \rightarrow Cl^- + HOBr$$

According to the method, hypobromite is produced by, (1) in case of directly using chlorine gas, reacting chlorine gas and water to generate hypochlorite and adding a bromide salt solution to the hypochlorite solution; or by, (2) in case of using hypochlorite, adding a bromide salt solution to a hypochlorite solution. Use of such combination of chlorine and bromide for controlling the microbial growth is also described in U.S. Pat. No. 3,795,271 granted to Saunier et al. In particular, as indicated by Trulear et al., "Recent Advances in Halogen Based Biocontrol." Corrosion, 1988, Vol. 19, 1-19, hypobromite is produced immediately before being applied to the cooling towers by injecting a sodium bromide solution into a supply line of a hypochlorite solution in a prescribed molar ratio. This application method of hypobromite is generally used to improve the production yield of hypobromite. If there is no mention that a bromide ion solution should be directly

added to the cooling towers, hypobromite is produced immediately before being applied to cooling towers by reacting hypochlorite with a sodium bromide solution. In addition, the '852 patent indicates that sulfamic acid should be used in higher amounts than a bromide ion.

In order to solve the volatile problem of hypobromite, sulfamic acid is used as a stabilzer, as described in patents granted to Dallmier et al., including U.S. Pat. Nos. 5,683,654, 5,795,487, 5,942,126, 6,136,205, etc., in which stabilized bromine is produced by primarily reacting a chlorine oxidant, that is, hypochlorite with a water-soluble bromide ion to generate hypobromite and reacting the hypobromite with sulfamic acid. However, the stabilized bromine, that is, bromosulfamate is limited in use economically although having higher disinfection efficacy than chlorosulfamate.

In addition, biocides comprising a bromide ion and stabilized chlorine instead of the stabilized bromine are disclosed in U.S. Pat. No. 6,037,318 granted to Na et al., U.S. Pat. No. 6,478,972 B1 (hereinafter, referred to as simply '972 patent) granted to Shim et al., and International Pat. Application No. KR03/00423. In the above patents except the '318 patent, hypobromite is produced by primarily reacting hypochlorite with sulfamic acid and reacting the generated stabilized chlorine with a bromide ion in an aqueous system. The '318 patent granted to Na et al. describes a method of preparing a bleaching composition comprising stabilized chlorine and a bromide ion.

U.S. Pat. No. 6,110,387 (hereinafter, referred to as simply '387 patent) describes a method for stabilizing bromine biocides in water, comprising adding a sufficient amount of a sulfamate source (0.25 to 2 millimoles per liter) and a sufficient amount of a bromide ion (0.34 to 2 millimoles per liter) to a swimming pool and then periodically introducing a chlorine oxidant to maintain an available bromine concentration in the range of 2 to 6 ppm in the swimming pool. Compared to chlorine biocides, according to the '387 patent, a sufficient sulfamate ion and a sufficient bromide ion is supplied to form stabilized bromine in water.

However, the '387 patent does not mention the nature of the produced biocidal bromine species.

On the other hand, when hypobromite is used as a biocide, decomposition of phosphonates such as 1,1-hydroxyethylidene diphosphonic acid (HEDP) is increased to an about two-fold degree, compared to the case of using hypochlorite as a biocide. According to the '852 patent, use of sulfamic acid as a stabilizer for hypobromite can reduce the decomposition of the phosphonates to the level of the case of using hypochlorite as a biocide.

Biocidal activity of chlorosulfamate produced by reaction of hypochlorite with sulfamic acid is described in detail by Delaney et al., "Bactericidal Properties of Chlorosulfamates", Proceeding of the American Society of Civil Engineers, Journal of the Sanitary Engineering Division Feb. 1972 (pp23), in which chlorosulfamates are mentioned to be not suitable for application to swimming pools.

The penetration of chlorosulfamate into microbial biofilms was reported by Stewart et al., "Biofilm Penetration and Disinfection Efficacy of Alkaline Hypochlorite and Chlorosulfamates", Journal of Applied Microbiology 2001, Vol. 91, 525-532. According to this report, chlorosulfamates penetrate into biofilms in the degree comparable to chloride ions, and can easily penetrate biofilms unlike general oxidizing biocides due to their low reactivity to biofilms, indicating their use as biocides for biofilm control.

Microbial contamination of aqueous systems can be also prevented, as described in U.S. Pat. No. 6,103,131 granted to McNeel et al., which discloses a method of inhibiting microorganisms to adhere to a submerged surface of an aqueous systems by coating the submergible surfaces of slides (glass or stainless steel) with sulfamic acid derivatives, or by introducing a constant amount of sulfamic acid derivatives into aqueous systems.

DISCLOSURE OF THE INVENTION

It is therefore an object of the present invention to provide a method of controlling microbial fouling with an improved anti-microbial fouling effect, which is based on the detachment of slime formed on a submerged surface simultaneously with killing of microorganisms in an aqueous system.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing dissociation of hypochlorite according to pH.

BEST MODES FOR CARRYING OUT THE INVENTION

In an aspect of the present invention, there is provided a method of controlling microbial fouling in an aqueous system, comprising adding a chlorine oxidant, a sulfamate ion source and a water-soluble bromide ion source to the aqueous system having a pH of 5 to 10 in an amount maintaining a total residual chlorine concentration of 1 to 9 ppm, in an amount maintaining a sulfamate ion concentration of 0.01 to 0.2 mmole/L (millimole per liter) and in an amount maintaining a water-soluble bromide ion concentration of 0.005 to 0.125 mmole/L, respectively, wherein the chlorine oxidant and the sulfamate ion source are used in a molar ratio of 1:20 or less.

In another aspect of the present invention, there is provided a method of killing microorganisms in an aqueous system, comprising the steps of adding a chlorine oxidant, a sulfamate ion source and a water-soluble bromide ion source to the aqueous system having a pH of 5 to 10; killing planktonic bacteria in the aqueous system by hypochlorite produced by the chlorine oxidant added to the aqueous system and/or hypobromite produced by reaction of the produced hypochlorite with the water-soluble bromide ion source added; detaching slime formed on a surface of an equipment or an apparatus in the aqueous system from the surface and dispering the slime by chlorosulfamate produced by reaction of the hypochlorite produced in the aqueous system with the sulfamate ion source

added and/or bromosulfamate produced by reaction of the chlorosulfamate with the water-soluble bromide ion source added; and killing sessile bacteria contained in the dispersed slime by the hypochlorite and/or the hypobromite and/or the bromosulfamate in the aqueous system.

Based on the fact that a variety of problems caused by microbial contamination in aqueous systems are produced mainly by slime formed by sessile bacteria, the present inventors studied methods capable of inhibiting slime formation in aqueous systems. This research resulted in the finding that chlorosulfamate produced by reaction of a chlorine oxidant with a sulfamate ion source has an effect of inhibiting microorganisms to adhere the surface of an equipment or an apparatus in the aqueous system although the high content of sulfamate leads to a decrease in antimicrobial efficacy, while bromosulfamate with a high oxidizing power is produced when a bromide ion source is added to the aqueous system containing the chlorosulfamate, thereby effectively detaching slime formed on a submerged surface and killing microorganisms contained the slime. Based on the above finding, the present inventors continued to study and completed the present invention.

Chlorosulfamate is produced by reaction of hypochlorite with sulfamate ion according to the following reaction formula.

$$NH_2SO_3^- \rightarrow NHClSO_3^- + H_2O$$

$$NHClSO_3^- \rightarrow NCl_2SO_3^- + H_2O$$

According to a report associated with the above reaction formula (Delaney et al., "Bactericidal Properties of Chlorosulfamates", Proceeding of the American Society of Civil Engineers, Journal of the Sanitary Engineering Division Feb. 1972, pp23), when sulfamic acid is chlorinated in a pH ranging from 5 to 8, monochlorosulfamate is difficult to be isolated because dichlorosulfamate is produced faster than monochlorosulfamate, while dichlorosulfamate is superior in disinfection efficacy to monochlorosulfamate.

In addition, disinfeciton efficacy of chlorosulfamate is increased along with an increase of pH.

Based on the fact that chlorosulfamate is not a single compound but a mixture of dichlorosulfamate and monochlorosulfamate, which have different properties from each other, hypochlorite and sulfamic acid were, in the present invention, reacted at various ratios and then added to an aqueous system, or individually added directly to the aqueous system and reacted therein. As a result, when the content of sulfamic acid was higher than that of hypochlorite, chlorosulfamate showed decreased microbicidal activity due to the higher production of monochlorosulfamate than dichlorosulfamate, whereas it retained the effects of penetrating into slime formed in the aqueous system and inhibiting microorganisms to adhere a submerged surface.

Typically, when bromide ion is reacted with hypochlorite to produce hypobromite before being added to an aqueous system, the bromide ion is not detected in the aqueous system. However, when the bromide ion is directly added to an aqueous system, the bromide ion still exists in the aqueous system even upon being added in smaller amounts than hypochlorite. The residual bromide ion penetrates into slime and reacts with chlorosulfamate therein, leading to detachment of the slime by forming bromosulfamate.

In accordance with the present invention, when a chlorine oxidant, a sulfamate ion source and a water-soluble bromide ion source are introduced into an aqueous system having a pH of 5 to 10, preferably 6.5 to 9.5, several oxidizing biocides having microbicidal activity are produced, including hypobromite, chlorosulfamate and bromosulfamate produced by reaction of chlorine with a bromide ion, reaction of hypochlorite with sulfamate and reaction of hypobromite with sulfamate, respectively. In addition, since the chlorine oxidant, sulfamate ion source and water-soluble bromide ion source are used in amounts within specific ranges, their slime penetration ability and microbicidal activity are suitably controlled, thereby effectively protecting the aqueous system from microbial fouling.

The present invention will be described in more detail, below.

The method of the present invention is applied to an aqueous system having a pH of 5 to 10, and preferably, 6.5 to 9.5.

The pH of an aqueous system to which the present method is applicable, that is, the degree of dissociation of hypochlorite affects production of hypobromite, chlorosulfamate and bromosulfamate in the aqueous system.

The degree of dissociation of hypochlorite that is a weak acid varies according to pH. With reference to Fig. 1, in a pH of below 5.0, hypochlorite is present as HOCl and Cl_2, while being just as OCl^- in a pH of over 10. Therefore, in an aqueous system containing hypochlorite, sulfamate ion and bromide ion, predominant biocides vary according to pH of the aqueous system, which may have different properties. In detail, in a pH of below 5, the reaction of the hypochlorite with the bromide ion is stimulated, and hypobromite production is thus increased, leading to increase of bromosulfamate production. The produced biocide has a a high oxidizing power, but is poor in penetrating into slime. In contrast, in a pH of over 10, the reaction of the hypochlorite with the water-soluble bromide ion is inhibited, and, thus, chlorosulfamate with low oxidizing power is mainly produced. The produced biocide has an excellent effect on penetration into slime, but have a poor microbicidal effect. Therefore, a pH range suitable for the method of the present invention is 5 to 10, and preferably, 6.5 to 9.5.

On the other hand, amounts of the chlorine oxidant, sulfamate ion source and water-soluble bromide ion source, used in the method of the present invention, are determined taking into consideration their effect on inhibition of slime attachment to a submerged surface and microbicidal effect in an aqueous system to be treated.

The chlorine oxidant is preferably used in an amount maintaining a total residual chlorine level of 1 to 9 ppm. In case that the total residual chlorine level is below 1 ppm, free residual halgen with a high oxidizing power is produced in relatively low amounts even in the presence of the bromide ion

source, and, thus, biocides with low biocidal activity are mainly produced. In contrast, in a total residual chlorine level of over 9 ppm, free residual halgen with a high oxidizing power is produced in relatively high amounts in the presence of the bromide ion source, and, thus, biocides with high biocidal activity are mainly produced. However, the excessive introduction of chlorine brings about an increase in the concentration of the chloride ion, which causes corrosion, as well as the consumption of the biocide is increased, leading economical problems.

In case of sulfamate, when sulfamate is added in very high amounts or the content of the sulfamate becomes higher than that of chlorine with time due to the consumption of chlorine by reaction of chlorosulfamate produced in an aqueous system with organic materials, biocides with low biocidal activity are mainly produced, where they retain an inhibitory activity against slime attachment to a submerged surface of an equipment or apparatus in the aqueous system. Therefore, it is sufficient that sulfamate is added in an amount of 0.2 mmole/L or less in an aqueous system. However, in a non-circulating aqueous system or circulating aqueous system with a low flow rate, over 0.01 mmole/L of sulfamate is required to obtain an inhibitory effect on slime attachment to a submerged surface.

On the other hand, it is preferred that the bromide ion source is added in an amount maintaining a water-soluble bromide ion concentration of 0.005 to 0.125 mmole/L. In case that the bromide ion concentration is below 0.005 mmole/L, free residual halogen with a high oxidizing power is formed at low levels, resulting in insufficient disinfection. In case that the bromide ion concentration exceeds 0.125 mmole/L, hypobromite production is increased in an aqueous system, and, thus, production of bromosulfamate with a high oxidizing power is elevated, resulting in increase of biocide consumption as well as discharging of a large quantity of unreacted bromide ions to blow-down water. Therefore, this case is uneconomical and contrary to the present object to inhibit microorganisms to adhere a submerged surface and detach slime formed on the surface.

In addition, it is required that the chlorine oxidant and sulfamate ion source are introduced into an aqueous system at a molar ratio of 1:20 or less. When the sulfamate ion source is used above the range, that is, over 20 in the molar ratio, the resulting biocides have reduced biocidal activity.

In more detail, biocidal properties of chlorosulfamate produced by reaction of hypochlorite with sulfamic acid are described by Delaney et al., "Bactericidal Properties of Chlorosulfamates" Proceeding of the American Society of Civil Engineers, Journal of the Sanitary Engineering Division Feb. 1972 (pp23). According to the report, the chlorosulfamate concentration capable of killing 99% of *E. coli* in a pH ranging from 7 to 8 is 1,000 mg/L (1,000 ppm). However, this level, which meets barely the criteria of biocides usable in swimming pools, is not suitable for the object of the present invention. In addition, the present invention limits available concentrations of total residual chlorine to 1 to 9 ppm through several experiments due to the following reasons: when the chlorine concentration is less than 1 ppm, free residual halogen with a high oxidizing power is formed at low levels even under the presence of a bromide ion source, resulting in insufficient disinfection; and, when the level of total residual chlorine is over 9 ppm, free residual halogen with a high oxidizing power is produced at high levels under the presence of a bromide ion source, resulting in improved disinfection. However, this case is uneconomical because of an increase in the concentration of chloride ion, caused by the excessively added chlorine, which causes corrosion, while consumption of biocides is increased.

The concentration of the bromide ion source, suitable for the object of the present invention limiting the concentration of the total residual chlorine to 1 to 9 ppm, ranges from 0.005 to 0.125 mmole/L, which is equal to 0.4 to 10 ppm when expressed in weight. When the bromide ion is added to an aqueous system at very low concentrations, free residual halogen with a high oxidizing power is formed at very low levels, resulting in insufficient disinfection. In contrast, in a bromide ion source concentration exceeding the range, the resulting biocides are highly consumed, while a large quantity of unreacted bromide ion is discharged to blow-

down water, which is costly. For these reasons, the above concentration of the bromide ion source was determined through experiments to be described in Examples, below.

On the other hand, according to the conventional methods for disinfecting cooling waters, typically, corrosion inhibitors, scale inhibitors and hypochlorite as a microbial biocide are individually introduced to the cooling waters. The present invention has an advantage, as follows: a sulfamate ion solution is prepared as by neutralization of sulfamic acid, and a water-soluble bromide ion solution is prepared using sodium bromide (NaBr), where each solution may be used in combination with components required for the prevention of corrosion and scale formation, while hypochlrorite is directly applicable to an aqueous system to be treated according to conventional methods without modification, if its amount to be added is determined.

Each component used in the method of the present invention will be described, below.

The chlorine oxidants may be selected from among chlorine, sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite or calcium hypochlorite, trichloroisocyanuric acid, sodium dichlorocyanuric acid, dichlorohydantoin, and mixtures thereof, and sodium hypochlorite and chlorine are preferred.

The sulfamate ion source useful in the present invention may be selected from the group consisting of sulfamic acid or salts thereof, such as sodium sulfamate, calcium sulfamate, ammonium sulfamate, and mixtures thereof, and sulfamic acid is preferred. The sulfamate salts are prepared by neutralization sulfamic acid with a base.

On the other hand, the bromide ion source useful in the present invention may include sodium bromide, calcium bromide, lithium bromide, chlorine bromide and bromine, and sodium bromide is preferred.

Examples of the corrosion inhibitors may include an anodic corrosion inhibitor, such as chromate, nitride, orthophosphate, silicate or molibdate, a

cathodic corrosion inhibitor such as zinc, polyphosphate or phosphonate, and a copper corrosion inhibitor, such as mercaptobenzothiazole, benzothiazole, or tolyltriazole. Useful are organophosphates and acryl polymers as the scale inhibitor. The organophosphates are exemplified by triethanolamine phosphate (TEAP), aminotrimethylene phosphonic acid (AMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), etc.

Examples of the acryl polymers may include acrylic homopolymers, acrylic copolymers, and acryl terpolymers.

The method of the present invention can be applied to any aqueous system using water. The aqueous system to which the method of the present invention can be applied includes, but are not limited to, cooling towers of buildings or factories, industrial water systems such as water systems used in paper-making processes, wastewater recycling systems or gas washer systems, freshwater systems using reverse osmosis membranes, gas scrubber systems, ponds and water slides.

The following examples are presented to illustrate further various aspect of the present invention, but are not intended to limit the scope of this invention in any aspect.

EXAMPLES

Sodium hypochlorite (NaOCl) solution was used as a biocide in the present Examples, which were added to an aqueous system, and an effective amount of chlorine was measured as 12 % by the DPD-FAS method. A 0.1% NaOCl solution was prepared by dilution. After an oxidizing halogen biocide was added to the aqueous system, the change of free residual halogen and total residual halogen concentrations with the passage of time was measured by the DPD-FAS method. The free residual halogen indicates HOCl, OCl^-, HOBr or OBr^-, and the level of combined residual halogen reacted with ammonia-containing organic materials was calculated by subtracting the free residual halogen level from the

total residual halogen level. In order to investigate the biocidal activity of biocides against microorganisms, after 48 hrs of incubation at 32°C, microorganism populations were counted using 3M Petrifilm (aerobic count plate) and percentage viability (viability %) of the microorganisms was calculated by an equation of (initial number-viable number)/initial number.

COMPARATIVE EXAMPLE: Comparison of biocidal compositions for their biocidal activity

In order to compare the biocidal activity of three biocidal compositions, which includes a hypochlorite; a hypochlorite and a sulfamate salt; and a hypochlorite, a sulfamate salt and a bromide ion, respectively, beaker tests were performed. River water (pH 7.8) was put into a beaker, and each biocidal composition was added to the water. Total residual halogen levels and viability of microorganisms were measured with time. The water was maintained at 30 °C, and contained 1.5×10^6 of microorganisms. Herein, natural river water was used not to limit microorganism species. The results are given in Table 1, below.

TABLE 1

Comparison of the biocidal compositions with various combinations of hypochlorite, sulfamate salt and bromide ion for total residual halogen levels and viability of microorganisms with time

Sample No.	Biocidal agent	Added amount	Total residual halogen (ppm)				Microbial viability (%)			
			5 min	1 hr	2 hrs	24 hrs	5 min	1 hr	2 hrs	24 hrs
1*	NaOCl	3.7 ppm	0.5	0.5	0.1	-	0.5	0.5	-	-
2	NaOCl	3.7 ppm	2.3	1.9	1.6	1.3	67	57	35	27
	$NH_2SO_3^-$	0.1 mmole/L								
3**	NaOCl	3.7 ppm	2.1	1.7	1.4	1.1	60	55	54	2
	$NH_2SO_3^-$	0.1 mmole/L								
	Br^-	0.05 mmole/L								

*: Since combined halogen is produced upon addition of only NaOCl, the total residual halogen level is equal to the free halogen level; and

**: The level of bromide ions remaining in water in the beaker after one day was detected as 2.2 ppm by ion chromatography.

In case of sample No. 1 containing only hypochlorite, this biocidal agent was found to have an excellent initial biocidal effect against microorganisms. In contrast, in this case, the concentration of free residual chlorine was reduced to below 0.1 ppm after one day, and was equal to the concentration of total residual chlorine because chlorosulfamate was not formed in sample No. 1 not treated with sulfamate ion. In sample No. 2 treating with the biocidal composition including a sulfamate salt, free residual chlorine was not detected, while only combined residual chlorine was detected. In sample No. 3, trace amounts of free residual halogen were detected. Compared to sample No. 1 treated with only hypochlorite, sample No. 2 treated additionally with the sulfamate salt showed remarkably increased microbial viability, whereas retaining a total residual chlorine concentration of 1.3 ppm even after one day. In the sample 3 treated with the biocial composition including the bromide ion, total residual chlorine was maintained to about 1.1 ppm even after one day, as well as biocidal ability was improved in comparison with sample No. 2. In sample No. 3, bromide ion remaining in water was detected as 2.2 ppm by ion chromatography, indicating that about 45% of the initial bromide ion was consumed. Taken together with the results of sample No. 3, the bromide ion was detected although chlorosulfamate remains in water, that is, under a measurable total residual chlorine concentration. Also, the result that microbicidal ability in sample No. 3 was remarkably increased compared to sample No. 2 not treated with the bromide ion indicates that chlorosulfamate and bromide ion do not react with each other in a short time but slowly react with each other in water.

In sample No. 2 treated with the sulfamate ion, free residual chlorine was not produced even though addition of NaOCl, while trace amounts of free residual halogen were detected in sample No. 3. These results demonstrate that chlorosulfamate is produced in water by reaction of the hypochlorite with the sulfamate ion. The amount of the produced chlorosulfamate can be expressed as the concentration of combined residual chlorine calculated by subtracting the free

residual chlorine level from the total residual chlorine level.

EXAMPLE 1: Microbial viability and inhibition of slime attachment to a submerged surface according to various concentrations of sulfamate ion

Beaker tests were performed to investigate microbial viability and inhibition of slime formation when water is treated with hypochlorite and bromide ion along with sulfamate ion of various concentrations. To prevent corrosion and scale formation, an organophosphate, 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), and a polymer were added to water in amounts of 6 and 10 ppm, respectively. The water was adjusted to pH 8±0.2, and maintained at 30±2°C. River water (bacterial density: 1,500,000 CFU (colony forming unit)/ml) was used in this test, which contained 40 ppm of calcium hardness (based on calcium carbonate) and 22 ppm of M-alkalinity (based on calcium carbonate). The river water was agitated at 30 rpm during this test, and covered with a vinyl product to prevent evaporation of water while being not completely closed to allow for air ventilation. A carbon steel coupon of 5×2×0.2 cm was dipped into the water in each beaker while hanged by a thread, and washed with acetone and dried before use. The degree of slime attachment to the carbon steel coupon was evaluated by visual inspection, and expressed as five grades (1: no detection of attached slime; 5: very high slime attachment).

Total residual halogen concentrations and the degree of the slime formation on the carbon steel; and microbial viability according to various concentrations of the sulfamate ion are given in the following Tables 2 and 3, respectively.

TABLE 2

Total residual halogen concentrations and the degree of slime attachment according to various concentrations of the sulfamate ion

Sample No.	$NH_2SO_3^-$ Conc. (mmole/L)	Total residual halogen (ppm)					Slime attachment					
		Day 1	2	3	4	5	1	2	3	4	5	8
4	0	<0.1	-	-	-	-	1	1	3	3	5	5
5	0.005	0.1	-	-	-	-	1	1	1	2	3	5
6	0.01	0.7	0.3	<0.1	-	-	1	1	1	2	4	4
7	0.05	1.5	0.9	0.5	0.1	-	1	1	1	1	2	3
8	0.1	1.7	0.9	0.4	0.1	-	1	1	1	1	2	2
9	0.2	1.9	1.1	0.5	0.1	-	1	1	1	1	1	1
10	0.85	2.2	1.6	0.8	0.3	0.1	1	1	1	1	1	1
11	1.25	2.4	1.8	1.1	0.8	0.3	1	1	1	1	1	1

Note: 1) The initial total residual chlorine level was 4ppm by NaOCl

2) Br^- was added to water in an amount maintaining a water-soluble bromide ion concentration of 0.02 mmole/L

TABLE 3

Microbial viability according to various concentrations of the sulfamate ion

Sample No.	$NH_2SO_3^-$ Conc. (mmole/L)	Microbial viability (%)					
		Day 1	2	3	4	5	6
4	0	<0.1	20	57	93	nc	nc
5	0.005	1	15	37	80	nc	nc
6	0.01	5	27	35	60	80	nc
7	0.05	15	10	15	9	14	35
8	0.1	24	18	17	12	8	27
9	0.2	31	20	11	18	20	36
10	0.85	35	17	8	5	12	31
11	1.25	53	47	34	31	38	42

Note: 1) The initial total residual chlorine level was 4ppm by NaOCl

2) Br^- was added to water in an amount maintaining a water-soluble bromide ion concentration of 0.02 mmole/L

3) The cases showing a microbial viability of below 1% (about 15,000 CFU/ml) were expressed as "-", while the cases showing a very high viability were expressed as "nc"

In the sample Nos. 4 and 5 not treated with the sulfamate or treated with a low amount of the sulfamate, respectively, few total residual halogen were detected after two days. Therefore, in these cases, there was no expectation for water disinfection provided by sulfamate ion or bromide ion. In contrast, obvious biocidal effectiveness of sulfamate ion and bromide ion was found in the sample Nos. 6 to 10. That is, as shown in Tables 2 and 3, compared to the sample Nos. 4 and 5, total residual halogen in the sample Nos. 6 to 10 was maintained for a

relatively longer period, resulted in a reduction of microbial viability, however the number of viable bacteria was still high. However, it was surprising that bacterial adherence to the carbon steel coupons is remarkably reduced although the high viability of bacteria. This effect obviously resulted from the reaction of the bromide ion with chlorosulfamate produced by a reaction of hypochlorite with the sulfamate ion. The chlorosulfamate production was determined by measuring combined residual chlorine levels.

With the passage of time, chlorosulfamate, which serves as an oxidizing biocide, is reduced in its oxidizing power, that is, its biocial activity against microorganisms because of a decrease in active chlorine concentrations, caused by the reaction of the chlorosulfamate with microorganisms or other organic materials. Also, the oxidizing power of chlorosulfamate is lowered when a sulfamate ion is present in higher concentrations than oxidizing chlorine, as described by the aforementioned literature published by Delaney. However, in sample No. 6 treated with over 0.01 mmole/L of sulfamate ion (along with 4 ppm of NaOCl and 0.02 mmole/L of Br^-), despite a slight reduction in the oxidizing power of chlorosulfamate with time, the inhibition of bacterial proliferation and slime attachment to the carbon steel coupons lasted long time. These results are believed to originate from the nature of monochlorosulfamate, but mechanisms related with the results have been not clearly identified.

In sample Nos. 4 and 5 treated with only hypochlorite or a trace amount of sulfamate ion, free residual chlorine, which may play an important role in inhibition of microbial proliferation and slime attachment to the carbon steel slices, was not maintained in sufficient amount, while the slime attached to the carbon steel coupons was remarkably increased after one week. Therefore, when the sulfamate ion was not added or added in a trace amount to water, combined residual halogen was not produced, while the inhibition of microbial adhesion to the surfaces of the carbon steel slices was not detected.

In the case that a sulfamate ion was present in an amount significantly higher than oxidizing chlorine, as in sample No. 11, measurable total residual

halogen lasted for long time in the water, while the inhibition of microbial adhesion to carbon steel coupon was improved. In contrast, microbial viability was increased. This case did not properly control the balance between biocidal activity and inhibitory activity against microbial adhesion to a submerged surface while improving only the inhibitory effect against the microbial adhesion. In addition, in this case, free residual halogen was not produced even under the presence of a bromide ion. Therefore, when a sulfamate ion source is added to an aqueous system in an amount much higher than a chlorine oxidant, the purpose of the present invention cannot be achieved, which is to develop a biocial composition having proper oxidizing power while retaining an effect of inhibit microorganisms to adhere to a submerged surface.

Based on the fact that chlorosulfamate is a mixture of dichlorosulfamate and monochlorosulfamate, as shown in Tables 2 and 3, when the concentration of sulfamate ion was higher than that of hypochlorite, the produced biocidal compounds were found to have decreased biocidal activity. However, in this case, an unexpected effect was obtained as follows: slime attachment to a submerged surface was effectively inhibited even in a low concentration of chlorosulfamate. This effect was greatly improved by addition of a bromide ion. In particular, based on the result that a bromide ion is present in water in a constant level even after seven days, it is believed that chlorosulfamate and bromide ions do not react with each other in a short time, whereas co-existing in water and slowly react with each other to produce bromosulfamate, thereby inhibiting slime attachment to a submerged surface and detaching slime from the surface. However, clear mechanisms related with this result have not been identified.

EXAMPLE 2: Microbial viability and inhibition of slime attachment to a submerged surface according to various concentrations of the bromide ion

In order to investigate microbial viability and the inhibition of slime attachment to a submerged surface according to various concentrations of bromide

ion, water was treated with various concentrations of bromide ion along with sulfamate ion and hypochlorite according to the same method as in the Example 1, and microbial viability and the degree of slime attachment to the carbon steel coupons were measured. The results are given in Tables 4 and 5, below.

TABLE 4

Total residual halogen levels and the degree of slime attachment to a submerged surface according to various concentrations of bromide ion

Sample No.	Added component	Amount (mmole/L)	Total residual halogen (ppm)					Slime formation					
			Day 1	2	3	4	5	1	2	3	4	5	8
12	$NH_2SO_3^-$	0.05	1.8	0.8	0.4	0.2	-	1	1	1	2	2	3
	Br^-	0.002											
13	$NH_2SO_3^-$	0.05	1.1	0.3	0.1	<0.1	-	1	1	1	2	3	3
	Br^-	0.005											
14	$NH_2SO_3^-$	0.05	0.8	0.2	0.1	0.1	-	1	1	1	2	2	3
	Br^-	0.01											
15	$NH_2SO_3^-$	0.05	0.7	0.1	-	-	-	1	1	1	1	1	2
	Br^-	0.05											
16	$NH_2SO_3^-$	0.05	0.6	<0.1	-	-	-	1	1	1	1	1	2
	Br^-	0.125											
17	$NH_2SO_3^-$	0.05	0.4	-	-	-	-	1	1	1	1	2	3
	Br^-	0.25											
18	$NH_2SO_3^-$	0.15	2.1	1.6	0.7	0.2	-	1	1	1	1	2	1
	Br^-	0.002											
19	$NH_2SO_3^-$	0.15	1.8	1.1	0.6	0.2	0.1	1	1	1	1	2	2
	Br^-	0.005											
20	$NH_2SO_3^-$	0.15	1.5	0.7	0.2	0.1	-	1	1	1	1	1	1
	Br^-	0.01											
21	$NH_2SO_3^-$	0.15	1.4	0.6	0.4	0.1	-	1	1	1	1	1	1
	Br^-	0.05											
22	$NH_2SO_3^-$	0.15	1.5	0.7	0.2	0.1	-	1	1	1	1	1	2
	Br^-	0.125											
23	$NH_2SO_3^-$	0.15	1.4	0.5	0.1	<0.1	-	1	1	1	1	1	3
	Br^-	0.25											

Note: 1) The initial total residual chlorine level was 4ppm by NaOCl.

2) Total residual halogen was measured as trace amounts, while being expressed as "-" in case of being unenumerative

TABLE 5

Microbial viability according to various concentrations of bromide ion

Sample No.	Added component	Amount (mmole/L)	Microbial viability (%)					
			Day 1	2	3	4	5	8
12	$NH_2SO_3^-$	0.05	33	15	20	13	22	40

	Br^-	0.002						
13	$NH_2SO_3^-$	0.05	10	3	4	8	11	20
	Br^-	0.005						
14	$NH_2SO_3^-$	0.05	1	2	1	6	9	15
	Br^-	0.01						
15	$NH_2SO_3^-$	0.05	-	-	1	1	2	5
	Br^-	0.05						
16	$NH_2SO_3^-$	0.05	-	-	1	1	1	2
	Br^-	0.125						
17	$NH_2SO_3^-$	0.05	-	-	-	10	22	41
	Br^-	0.25						
18	$NH_2SO_3^-$	0.15	20	15	17	23	38	54
	Br^-	0.002						
19	$NH_2SO_3^-$	0.15	12	4	7	3	1	5
	Br^-	0.005						
20	$NH_2SO_3^-$	0.15	3	1	-	1	8	22
	Br^-	0.01						
21	$NH_2SO_3^-$	0.15	1	-	4	9	13	15
	Br^-	0.05						
22	$NH_2SO_3^-$	0.15	3	-	5	4	11	20
	Br^-	0.125						
23	$NH_2SO_3^-$	0.15	3	-	1	4	2	15
	Br^-	0.25						

Note: 1) The initial total residual chlorine level was 4ppm of NaOCl

2) The cases showing a microbial viability of below 1% (about 15,000 CFU/ml) were expressed as "-"

When a bromide ion source was added to water in a relatively very low amount of 0.002 mmole/L in comparison with NaOCl, as in the sample Nos. 12 and 18, measurable total residual halogen was maintained until 4th day, while slime attachment to the carbon steel slices was inhibited. In contrast, the improved biocidal activity by addition of bromide ion was not observed. However, when 0.05 mmole/L of sulfamate ion, corresponding to about 10% of the amount of the added chlorine, as shown in Tables 4 and 5, microbial viability was remarkably reduced while inhibition of microbial adhesion to the carbon steel slices was maintained. When the amount of the bromide ion added was increased, the effects of killing microorganisms and inhibiting microbial adhesion to the carbon steel slices were improved in a disproportional manner to the amount of the bromide ion added. In this case of increasing the amount of bromide ion, the initial biocidal activity was improved, while measurable total residual halogen was maintained for a shorter period. In particular, in cases of adding excessive

bromide ion to water, as in the sample Nos. 17 and 23, high initial microbicidal activity was observed. However, in this case, measurable total residual halogen was maintained for just about two days, while the inhibitory effect versus microbial adherence to the carbon steel slices was reduced with time. Taken together, when the amount of bromide ion is increased, the produced biocidal compounds have mainly biocidal activity, rather than a balanced effect between the biocial activity and the inhibition activity versus the microbial adhesion to the coupons. Therefore, in the case of increasing the amount of bromide ion, disinfection efficacy is high at a early stage but reduced with the passage of time, leading to a high consumption of the biocides and increased use of the expensive bromide, while the inhibition of slime attachment to a submerged surface is reduced. Thus, this case is not suitable for the purpose of the present invention.

EXAMPLE 3: Microbial viability and inhibition of slime attachment to a submerged surface according to various concentrations of hypochlorite

In order to investigate microbial viability and inhibition of slime attachment to a submerged surface according to various concentrations of hypochlorite, water was treated with various concentrations of hypochlorite along with a sulfamate ion and bromide ion according to the same method as in the Example 1, and microbial viability and the degree of slime attachment to the carbon steel coupons were measured. The results are given in Tables 6 and 7, below.

TABLE 6

Total residual halogen levels and the degree of slime attachment to a submerged surface according to various concentrations of hypochlorite

Sample No.	Added component	Amount (mmole/L)	Total residual halogen (ppm)					Slime attachment					
			Day 1	2	3	4	5	Day 1	2	3	4	5	8
24	$NH_2SO_3^-$	0.05	-	-	-	-	-	1	1	2	4	5	5

	NaOCl	0.5 ppm											
25	$NH_2SO_3^-$	0.05	0.1	-	-	-	-	1	1	1	2	3	5
	NaOCl	1 ppm											
26	$NH_2SO_3^-$	0.05	0.5	0.2	-	-	-	1	1	1	2	2	3
	NaOCl	2 ppm											
27	$NH_2SO_3^-$	0.05	0.8	0.2	0.1	-	-	1	1	1	1	1	2
	NaOCl	4 ppm											
28	$NH_2SO_3^-$	0.05	4.5	3.8	2.8	1.9	1.3	1	1	1	1	1	1
	NaOCl	8 ppm											
29	$NH_2SO_3^-$	0.05	6.4	5.4	4.3	3.9	3.1	1	1	1	1	1	1
	NaOCl	9 ppm											
30	$NH_2SO_3^-$	0.05	7.1	6.2	5.2	4.7	4.1	1	1	1	1	1	1
	NaOCl	11 ppm											
31	$NH_2SO_3^-$	0.15	-	-	-	-	-	1	1	2	3	5	5
	NaOCl	0.5 ppm											
32	$NH_2SO_3^-$	0.15	0.3	0.1	-	-	-	1	1	1	2	3	4
	NaOCl	1 ppm											
33	$NH_2SO_3^-$	0.15	0.7	0.3	0.1	-	-	1	1	1	1	2	4
	NaOCl	2 ppm											
34	$NH_2SO_3^-$	0.15	1.7	0.6	0.2	0.1	-	1	1	1	1	1	1
	NaOCl	4 ppm											
35	$NH_2SO_3^-$	0.15	5.9	5.2	4.6	4.1	3.5	1	1	1	1	1	1
	NaOCl	8 ppm											
36	$NH_2SO_3^-$	0.15	6.7	6.1	5.5	4.9	4.0	1	1	1	1	1	1
	NaOCl	9 ppm											
37	$NH_2SO_3^-$	0.15	7.2	6.3	5.7	5.1	4.2	1	1	1	1	1	1
	NaOCl	11 ppm											

Note: 1) Br^- was added to water in an amount of 0.05 mmole/L

2) Total residual halogen was measured as trace amounts, while being expressed as "-" in case of being unenumerative

TABLE 7

Microbial viability according to various concentrations of hypochlorite

Sample No.	Component	Amount (mmole/L)	Microbial viability (%)					
			Day 1	2	3	4	5	8
24	$NH_2SO_3^-$	0.05	95	nc	nc	nc	nc	nc
	NaOCl	0.5 ppm						
25	$NH_2SO_3^-$	0.05	70	75	73	80	85	nc
	NaOCl	1 ppm						
26	$NH_2SO_3^-$	0.05	32	35	40	38	70	-
	NaOCl	2 ppm						
27	$NH_2SO_3^-$	0.05	1	2	3	2	3	12
	NaOCl	4 ppm						
28	$NH_2SO_3^-$	0.05	-	-	-	1	-	2
	NaOCl	8 ppm						
29	$NH_2SO_3^-$	0.05	-	-	-	-	-	-
	NaOCl	9 ppm						
30	$NH_2SO_3^-$	0.05	-	-	-	-	-	-
	NaOCl	11 ppm						
31	$NH_2SO_3^-$	0.15	90	nc	nc	nc	nc	nc
	NaOCl	0.5 ppm						

32	$NH_2SO_3^-$	0.15	62	58	70	70	nc	nc
	NaOCl	1 ppm						
33	$NH_2SO_3^-$	0.15	28	40	38	43	51	-
	NaOCl	2 ppm						
34	$NH_2SO_3^-$	0.15	4	-	2	3	2	8
	NaOCl	4 ppm						
35	$NH_2SO_3^-$	0.15	-	-	-	-	-	3
	NaOCl	8 ppm						
36	$NH_2SO_3^-$	0.15	-	-	-	-	-	-
	NaOCl	9 ppm						
37	$NH_2SO_3^-$	0.15	-	-	-	-	-	-
	NaOCl	11 ppm						

Note: 1) Br^- was added to water in an amount of 0.05 mmole/L

2)The cases showing a microbial viability of below 1% (about 15,000 CFU/ml) were expressed as "-", while the cases showing a very high viability were expressed as "nc"

As in the sample Nos. 24 and 31, when hypochlorite was added to water in an amount below 1 ppm, the expected biocidal activity of the added components was not observed, while microbial adherence to the carbon steel slices was rarely inhibited. However, when the concentration of hypochlorite was increased, microbial activity was remarkably enhanced, while inhibition of slime attachment to the slices was also increased. In the sample Nos. 25 and 32, despite trace amounts of total residual halogen and high microbial viability after one day, slime attachment to the carbon steel slices was remarkably reduced until the 5th day, compared to the sample Nos. 24 and 31. These results were similar those in the '131 patent granted to MacNeel et al., but mechanisms related with the results were not clearly identified. When the concentration of NaOCl, microbial viability was greatly reduced, while microbial adherence to the slices was remarkably inhibited, resulting in few microbial adherences to the slices even after eight days. When NaOCl was added to water in an amount of over 10 ppm, as in the sample Nos. 30 and 37, microbial viability was remarkably reduced, while slime attachment to the slices was rarely observed. In this case, since hypochlorite was added to water in an amount higher than sulfamate ion, a part of the hypochlorite added did not participate in the reaction with sulfamate ion, and total and free residual chlorine was thus produced, resulting in high biocidal activity and inhibitory activity versus

slime attachment to the slices. However, this case is problematic as follows: excessive hypochlorite brings out unpleasant odors by volatilization of unreacted hypochlorite; and excessive chloride ions stimulate corrosion.

EXAMPLE 4: Microbial viability and inhibition of slime attachment to a submerged surface according to pH

The river water was treated with hypochlorite, sulfamate ion and bromide ion under the same condition as in sample No. 1 except for pH of the water, total residual halogen levels, slime attachment to the carbon steel coupons and microbial viability were measured. The results are given in Tables 8 and 9, below.

TABLE 8

Total residual halogen levels and the degree of slime attachment to a submerged surface according to pH

Sample No.	pH	Total residual halogen (ppm)					Slime attachment					
		Day 1	2	3	4	5	1	2	3	4	5	8
38	5	1.0	0.2	-	-	-	1	1	1	3	4	5
39	6	1.5	0.8	0.1	-	-	1	1	1	2	2	3
40	7	2.1	1.2	0.3	-	-	1	1	1	1	1	2
41	8	2.9	1.7	1.1	0.5	0.2	1	1	1	1	1	1
42	9	3.7	2.8	2.2	1.8	1.2	1	1	1	1	1	1
43	10	4.2	3.6	3.0	2.1	1.9	1	1	1	1	1	1

Note: 1) NaOCl, $NH_2SO_3^-$ and Br^- were added to water in amounts of 6 ppm, 0.1 mmole/L and 0.01 mmole/L, respectively

2) Total residual halogen was measured as trace amounts, while being expressed as "-" in case of being unenumerative

TABLE 9

Microbial viability according to pH

Sample No.	pH	Slime attachment state					
		Day 1	2	3	4	5	8

38	5	-	-	-	10	40	nc
39	6	-	-	2	6	20	45
40	7	-	-	-	-	3	5
41	8	-	-	-	-	1	1
42	9	5	2	6	5	7	8
43	10	20	15	25	30	23	25

Note: 1) NaOCl, $NH_2SO_3^-$ and Br^- were added to water in amounts of 6 ppm, 0.1 mmole/L and 0.01 mmole/L, respectively

2) The cases showing a microbial viability of below 1% (about 15,000 CFU/ml) were expressed as "-", while the cases showing a very high viability were expressed as "nc"

As shown in Tables 8 and 9, in a low pH, despite the presence of sulfamate, total residual halogen was rapidly reduced, while microbial viability was remarkably reduced. However, after three days, slime began to be formed by increased microbial proliferation. In a high pH, microbial viability was slightly increased compared to the cases of low pH, while total residual halogen was maintained even after one week. In particular, in a pH of 10, microbial viability was remarkably increased despite high concentrations of total residual halogen, whereas inhibition of microbial attachment to the carbon steel coupons was increased. However, these results were contrary to the report published by Delaney et al., in which chlorosulfamate has excellent microbicial activity in a high pH. These different results are believed to originate from the addition of bromide ion, but the related mechanisms have been not clearly identified. However, the different results can be explained, as follows: in water of a low pH, bromide ion reacts with chlorosulfamate or hypochlorite to produce bromosulfamate with a high oxidizing power, and this case thus provide biocides with high biocidal activity, resulting in the rapid consumption of chlorosulfamate; and in a high pH, since the reaction rate of the bromide ion with chlorosulfamate is reduced, a biocial compound with high biocidal activity was formed at relatively low levels, while slime was not formed on a submerged surface despite high microbial viability, where the number of viable microorganisms was not further increased with the passage of time.

EXAMPLE 5

Based on the results obtained in the above beaker tests, pilot cooling tower tests were conducted. A pilot cooling tower was prepared, which has a water capacity of 120kg and a water flow rate of 1,600 kg/hr. The pH of water was controlled within ±0.2 from the target pH value. The temperature difference through the cooling tower was 5℃. The cycle of concentration was maintained at 6 by controlling below-down amount of water to 2.8 kg/hr. In addition, PBTC and a polymer were continuously added to the water to a level of 6 and 10 ppm, respectively, to prevent corrosion and scaling of the carbon steel slices. The pilot cooling tower was maintained at 35±2°C. To use naturally occurring microorganisms, river water was used, which had 40 ppm of calcium hardness (based on calcium carbonate) and 22 ppm of M-alkalinity (based on calcium carbonate) and contained microorganisms of 1.8×10^6 CFU/ml. The pH of the river water was adjusted to the test range with diluted sulphuric acid and caustic soda solution. The turbidity of the water was measured using the Hach's DR-2010, and expressed as FAU (Formazin Attenuation Units). Sulfamate ions and bromide ions were initially added in prescribed amounts to the water, and then continuously added to the water individually in combination with PBTC and the polymer in order to maintain desired concentrations in the water, taking into consideration the amounts of their loss. Hypochlorite was continuously injected into the water by a pump, based on the water flow rate.

In order to investigate slime removal from the pilot cooling tower, first, a corrosion inhibitor and a scale inhibitor were added to the water for four days to allow slime formation in the pilot cooling tower. Typically, when a non-ionic dispersing agent or an excessive biocide is introduced into an aqueous system with high microbial contamination, slime is removed while the turbidity of the aqueous system is increased. Based on this phenomenon, biocial compositions were added to the pilot cooling tower, and the water was evaluated for change in turbidity,

change in residual halogen concentrations and microbial viability. After completing the test, slime removal from the pilot cooling tower was determined by directly investigating the degree of microbial contamination in the pilot cooling tower. The results are given in Table 10, below, in which the results are expressed as three grades: 1: no detection; 2: a little; and 3: plenty. The grade 1 means the case in that no slime is detected in the pilot cooling tower by visual examination and by hands. The grade 2 means the case in that no slime is visually detected while slime is sensed by hands. The grade 3 means the case in that slime is visually detected.

TABLE 10

Water turbidity, the number of viable microorganisms, the degree of slime removal and total residual halogen levels in the pilot cooling tower

Sample No.	pH	Added amount (mmole/L)												
		NaOCl	Br^-	$NH_2SO_3^-$	Day 0	1	2	3	4	5	6	7	8	9	10
P-0	8	0.1ppm	-	-											
		Turbidity (FAU)			18	16	12	9	11	8	9	9	8	9	9
		No. of viable microorganisms (CFU)			nc	10^3	10^3	10^3	10^2	10^1	10^2	10^2	10^2	10^2	10^2
		The degree of slime removal													3
		Free residual halogen			-	-	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.1	0.2
P-1	6	0.1ppm	0.05	0.1											
		Turbidity (FAU)			18	14	13	9	11	12	13	12	12	10	10
		No. of viable microorganisms (CFU)			nc	10^5	10^4	10^3	10^4	10^4	10^4	10^3	10^3	10^2	10^3
		The degree of slime removal													2
		Total residual halogen			-	-	0.1	0.1	0.2	0.7	0.9	1.2	1.3	1.1	0.9
P-2	7	0.1ppm	0.05	0.1											
		Turbidity (FAU)			16	14	13	9	11	24	20	15	12	11	11
		No. of viable microorganisms (CFU)			nc	10^5	10^4	10^3	10^2	10^6	10^5	10^3	10^2	10^3	10^4
		The degree of slime removal													1
		Total residual halogen			-	-	0.1	0.1	0.2	-	-	0.4	0.7	1.4	2.1
P-3	8	0.1ppm	0.05	0.1											

		Turbidity (FAU)	17	15	15	29	17	15	17	15	12	12	12
		No. of viable microorganisms (CFU)	nc	10^3	10^4	nc	10^6	10^3	10^2	10^3	10^2	10^2	10^3
		The degree of slime removal											1
		Total residual halogen	-	-	-	-	-	0.5	1.4	1.9	2.4	2.8	3.1
P-4	9	0.1ppm | 0.05 | 0.1											
		Turbidity (FAU)	18	14	13	9	11	22	20	18	12	11	11
		No. of viable microorganisms (CFU)	nc	10^5	10^4	10^3	10^4	10^6	10^6	10^4	10^4	10^4	10^4
		The degree of slime removal											1
		Free residual halogen	-	-	-	0.5	0.7	-	-	0.9	1.2	3.7	3.8
P-5	10	0.1ppm | 0.05 | 0.1											
		Turbidity (FAU)	18	14	13	9	11	13	15	14	15	15	13
		No. of viable microorganisms (CFU)	nc	10^5	10^4	10^4	10^5	10^4	10^5	10^5	10^5	10^4	10^4
		The degree of slime removal											2
		Total residual halogen	1.5	2.3	2.7	3.1	2.9	1.7	2.6	3.1	3.2	4.6	4.3
P-6	8	0.2ppm | 0.05 | 0.1											
		Turbidity (FAU)	18	38	25	17	11	12	10	11	10	9	10
		No. of viable microorganisms (CFU)	nc	nc	10^6	10^4	10^2	10^1	10^1	10^2	10^1	10^0	10^0
		The degree of slime removal											1
		Total residual halogen	-	-	-	1.1	2.9	3.7	4.6	5.1	5.6	5.3	5.4
P-7	8	0.1ppm | 0.1 | 0.2											
		Turbidity (FAU)	17	15	19	22	17	11	12	10	9	10	11
		No. of viable microorganisms (CFU)	nc	10^5	10^6	nc	10^5	10^3	10^4	10^3	10^3	10^4	10^3
		The degree of slime removal											1
		Total residual halogen	-	-	-	1.1	2.9	3.7	4.6	5.1	5.6	5.3	5.4
P-8	8	0.1ppm | 0.05 | 0.2											
		Turbidity (FAU)	18	16	17	18	23	16	14	14	13	15	13
		No. of viable microorganisms (CFU)	nc	10^4	10^6	10^6	10^5	10^3	10^1	10^2	10^1	10^2	10^2
		The degree of slime removal											1
		Total residual halogen	-	-	-	-	-	-	0.6	1.1	1.5	2.8	4.1

Note: 1) NaOCl was continuously added to water in a prescribed concentration (ppm) based on the amount of circulating water

2) Br^- and $NH_2SO_3^-$ were primarily added to water based on the water capacity before the test, and then continuously added in combination of a corrosion inhibitor and a scale inhibitor based on the output water amount

3) Total residual halogen was measured as trace amounts, while being expressed as "-" in case of being unenumerative

4) The cases showing a very high microbial viability were expressed as "nc"

In case that the pilot cooling tower was treated according to a method common in the art, as in sample No. P-0, the concentration of free residual chlorine was 0.1-0.2 ppm that is very satisfactory in disinfecting water. Also, in this case, slime was not detected visually in the mock cooling tower, except for a part of the inner region with low flow rates and the edge region of the cooling tower. However, when the regions with low flow rates and the inner region of the cooling tower were handled by hands, sliminess was observed, which indicated slime formation. In contrast, when water was treated additionally with sulfamate ion and bromide ion, slime formation was not visually detected in the regions with low flow rates of the pilot cooling tower. Especially in the sample Nos. P-2, P-3 and P-4 in optimal pH values, slime formation was not detected visually and sensorially in any region of the pilot cooling tower.

In addition, as apparent from the results of the sample Nos. P-1 and P-5, in a low pH, the reactions of the hypochlorite, sulfamate ions and bromide ions added resulted in the increased production of hypobromite and bromosulfamate with a high oxidizing power. In contrast, in a high pH, chlorosulfamate with low oxidizing power and unreacted bromide ion were produced. Therefore, in case of water of a low pH, since hypochlorite and bromosulfamate with a high oxidizing power are produced at relatively high levels, biocidal activity against planktonic bacteria is maintained, whereas consumption of active halogen is increased. In contrast, in case of water of a high pH, since chlorosulfamate with low oxidizing power and unreacted bromide ion are predominantly produced, relatively low consumption of active halogen leads to high concentrations of total residual halogen, resulting in the inhibition of slime attachment to a submerged surface and penetration into the slime of the biocidal compounds last for longer periods, whereas the biocidal compounds have weak microbicidal activity. In a pH of below 6, total residual halogen was rarely detected. In a pH of over 10, although

total residual halogen was maintained at high levels since the reaction of chlorosulfamate and bromide ion is remarkably reduced, as in the sample Nos. P-1 and P-5, in the regions with low flow rates of the pilot cooling tower, slime was not detected visually but detected physically.

When the amount of hypochlorite was increased, as in sample No. P-6, total residual halogen was maintained at high levels, while the number of viable microorganisms was detected as below 10^2 cfu. Moreover, even after the test, no slime was formed in the pilot cooling tower. Also, free residual halogen was not detected at the early stage, but maintained to about 0.2 ppm after about five days. Further, there were not unpleasant odors that are generated upon using excessive hypochlorite.

In the sample Nos. P-7 and P-8 treated with relatively high amounts of sulfamate, total residual halogen was maintained at high levels for the test period, while the number of viable microorganisms was as slightly high as 10^4 cfu. When the amount of bromide ions was increased, the number of viable microorganisms was reduced to 10^2 cfu, whereas total residual halogen was maintained at low levels. These results originate from that the increase of the bromide ion concention leads to stimulate production of hypobromite and bromosulfamate with a high oxidizing power.

As shown in Table 10, the microbial number was increased with the increase of water turbidity. This increase in water turbidity was caused by the detachment of slime accumulated in the mock cooling tower. At states of high turbidity, total residual halogen was not detected. However, after the turbidity decreased, total residual halogen concentrations were gradually increased, and constantly maintained with the passage of time. These results were absolutely different from those of the sample Nos. P-0 treated with only hypochlorite.

With water with high turbidity, the microbial populations were enumerated using 3M™ Petrifilm plates and Mikroconut's dip-slides. The results of the two kinds of tests were different from each other. That is, the microbial number obtained using the Petrifilm plates was over 10-fold higher than that

obtained by the dip-slide tests. Also, a different pattern was observed in microbial growth. That is, when microorganisms were grown on Petrifilm plates, colony formation was rarely observed within one day, whereas being greatly increased after one or two days. This pattern in colony formation was quite different from previous patterns, but the cause of the results has been not identified.

INDUSTRIAL APPLICABILITY

As described hereinbefore, the method of the present invention is effective in inhibiting attachment to a submerged surface of microbial slime formed by mainly sessile bacteria in an aqueous system, as well as in killing bacteria contained in the slime and planktonic bacteria.

CLAIMS

1. A method of controlling microbial fouling in an aqueous system, comprising

adding a chlorine oxidant, a sulfamate ion source and a water-soluble bromide ion source to the aqueous system having a pH of 5 to 10 in an amount maintaining a total residual chlorine concentration of 1 to 9 ppm, in an amount maintaining a sulfamate ion concentration of 0.01 to 0.2 mmole/L (millimole per liter) and in an amount maintaining a water-soluble bromide ion concentration of 0.005 to 0.125 mmole/L, respectively,

wherein the chlorine oxidant and the sulfamate ion source are used in a molar ratio of 1:20 or less.

2. A method of killing microorganisms in an aqueous system, comprising

adding a chlorine oxidant, a sulfamate ion source and a water-soluble bromide ion source to the aqueous system having a pH of 5 to 10;

killing planktonic bacteria in the aqueous system by hypochlorite produced by the chlorine oxidant added to the aqueous system and/or hypobromite produced by reaction of the produced hypochlorite with the water-soluble bromide ion source added;

detaching slime formed on a surface of an equipment or an apparatus in the aqueous system from the surface and dispersing the slime by chlorosulfamate produced by reaction of the hypochlorite produced in the aqueous system with the sulfamate ion source added and/or bromosulfamate produced by reaction of the chlorosulfamate with the water-soluble bromide ion source added; and

killing sessile bacteria contained in the dispersed slime by the hypochlorite and/or the hypobromite and/or the bromosulfamate in the aqueous system.

3. The method as set forth in claim 1 or 2, wherein the chlorine oxidant,

the sulfamate ion source and the water-soluble bromide ion source are individually added to the aqueous system, or the water-soluble bromide ion source and the sulfamate ion source are added to the aqueous system after being premixed.

4. The method as set forth in claim 1 or 2, wherein the chlorine oxidant is selected from the group consisting of alkali or alkali earth metal hypochlorite salts, dichlorocyanuric acid, trichloroisocyanuric acid, bromochlorohydantoin, dichlorohydantoin, chlorine and mixtures thereof.

5. The method as set forth in claim 1 or 2, wherein the sulfamate ion source is selected from the group consisting of sulfamic acid or salts thereof which are sodium sulfamate, calcium sulfamate, ammonium sulfamate, and mixtures thereof.

6. The method as set forth in claim 1 or 2, wherein the bromide ion source is selected from the group consisting of sodium bromide, calcium bromide, potassium bromide, chlorine bromide, bromine, and mixtures thereof.

7. The method as set forth in claim 1 or 2, wherein the aqueous system has a pH of 6.5 to 9.5.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/26044

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C02F 1/50

US CL : 210/755

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/755, 754, 756, 764; 162/161; 422/37; 424/661,723

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,662,940 A (HIGHT et al.) 02 September 1997, col. 3 lines 1-55, and col. 9 line 22 through col. 10 line 2	1-7
A	US 6,478,972 B1 (SHIM et al.) 12 November 2002	
A	US 6,110,387 A (CHOUDHURY et al.) 29 August 2000	
A	US 5,942,126 A (DALLMIER et al.) 24 August 1999	
A	US 6,270,722 B1 (YANG et al.) 07 August 2001	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 December 2004 (06.12.2004)	30 DEC 2004
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Peter A. Hruskoci Telephone No. 571-272-0987

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